Narrow dispersed linear polyethylene using cobalt catalysts bearing cycloheptyl-fused bis(imino)pyridines; probing the effects of *ortho*-benzhydryl substitution

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Abstract

The cycloheptyl-fused cobalt(II) chloride complexes, [2,3:5,6-{C₄H₈C(N(2-R¹-4-R²-6-(CHPh₂)C₆H₂))₂C₅HN]CoCl₂ (R¹ = R² = Me **Co1**, R¹ = Me, R² = CHPh₂ **Co2**, R¹ = Et, R² = CHPh₂ **Co3**, R¹ = *i*-Pr, R² = CHPh₂ **Co4**, R¹ = Cl, R² = CHPh₂ **Co5**, R¹ = CHPh₂, R² = *i*-Pr **Co6**, R¹ = CHPh₂, R² = *t*-Bu **Co7**, R¹ = CHPh₂, R² = F **Co8**), have been prepared by a one-pot template approach. The molecular structures of **Co1**, **Co6** and **Co8** highlight the varying degrees of steric protection of the metal center imposed by the *ortho*-benzhydryl/-R¹ group pairing. On activation with either MAO or MMAO, **Co1** - **Co5** collectively displayed high activity (up to 2.87 × 10⁶ g (PE) mol⁻¹ (Co) h⁻¹ at 40 °C) affording highly linear low molecular weight polyethylene (*M_w* range: 12.8 - 59.4 kg mol⁻¹) with narrow polydispersities (*M_w*/*M_n* range: 1.4 – 2.7). End-group analysis of the polymers highlights the importance of both β-H elimination and chain transfer to aluminum as termination pathways. In relative terms, MMAO proved a marginally more effective activator than MAO with the catalytic activity, in either case, falling in the order: **Co1** > **Co5** > **Co2** > **Co3** > **Co4**. In marked contrast, the 2,6-(CHPh₂)₂-substituted precatalysts, **Co6**, **Co7** and **Co8** gave, in the presence of same aluminoxane activators, only trace amounts of polyethylene.

Keywords: Cobalt; coordination-insertion polymerization; linear polyethylene; β-H elimination; catalytic activity.

Introduction

Ever since the first disclosures of highly active homogeneous iron and cobalt catalysts for ethylene polymerization some twenty years ago, there has been a considerable drive to not only improve the performance characteristics of the catalyst but also broaden the range of polyolefinic materials.^{1,2} In terms of ligand support, the bis(imino)pyridine family has provided the benchmark framework that, through structural modification, allows control of both the catalyst activity and molecular weight of the polymer (**A**, Chart 1).³⁻²¹ Elsewhere, alternative *N,N,N* ligand sets have also emerged as compatible supports for both iron and cobalt catalysts such as 2,9-bis(imino)-1,10-phenanthrolines,²²⁻²⁷ 2-benzimidazol-6-imino-pyridines,²⁸⁻³¹ *N*-((pyridin-2-yl)methylene)-8-iminoquinolines³² and 2,8-bis(imino)quinolines.³³ As a general feature to all these classes of catalyst is the ability to control the polymerization performance through the substitution pattern of the imine *N*-aryl groups. Specifically, sterically bulky groups at the *ortho*-positions promote chain propagation and activity while the electronic properties of the *para*-group can have some influence on catalytic activity.^{12-13,16-17}

More recent developments have seen the emergence of ring-strain adjustable cycloalkyl-fused bis(imino)pyridines that allow an additional means of modulating activity and polymer molecular weight of not only iron and cobalt catalysts but also chromium (**B** – **E**, Chart 1).³⁴⁻⁴⁷ With particular regard to cobalt catalysts, the cyclohexyl-containing **B**³⁵ shows reasonable activity generating highly linear polyethylene waxes and oligomers. On the other hand, cycloheptyl-**C** (Ar = 2,6-Me₂Ph, 2,6-Et₂Ph, 2,6-*i*-Pr₂Ph, 2,4,6-Me₂Ph, 2,6-Et₂-4-MePh), are generally more productive and afford solely low molecular weight polyethylene.⁴¹ With regard to the largest ring system **D**,⁴⁵ high activity is again exhibited while the polyethylenes attain the highest molecular weight for the **B** - **D** series forming strictly linear polymer chains.

Within a fused ring family, further modulation of the molecular weight can be achieved by varying the steric properties of the *N*-aryl *ortho*-substituents. For example, for the cycloheptyl-containing cobalt complexes, **C**, the most sterically encumbered example (Ar = 2,6-*i*-Pr₂Ph) forms

the highest molecular weight polymer of this class. By comparison, cobalt precatalysts **E** (Chart 1),⁴⁶ incorporating even more bulky *ortho*-cycloalkyl substituents, generate even higher molecular weight polyethylene of narrow dispersity. Conversely, the cycloheptyl-fused **F**-type complexes (Chart 1) bearing *N,N,O*-ligands, serve as precatalysts for ethylene oligomerization with good α -olefin selectivity.⁴⁸

Chart 1 Fused-cycloalkyl *N,N,N*- and *N,N,O*-complexes derived from **A**

In this work, we return to the bis(imino)-2,3:5,6-bis(pentamethylene)pyridine family of cobalt precatalysts (**C** or **E**, Chart 1) with a view to explore the effects of benzhydryl (CHPh₂) substitution on catalytic performance in ethylene polymerization. Indeed, incorporation of such sterically enhanced alkyl groups have been reported to impart some notable beneficial effects in related *N,N,N*-catalysts, including on catalyst activity, molecular weight and thermal stability.^{10,46} In particular, we describe the synthesis, characterization and catalytic evaluation (using two different co-catalysts) of a series of cobalt complexes of type **G** (Chart 1), in which at least one *ortho*-site of each *N*-aryl group is appended by a CHPh₂ group. In addition, the effect of introducing chloride, smaller alkyl groups (R¹ = Me, Et, *i*-Pr) and CHPh₂ at the remaining *ortho*-position is explored, while the *para*-position is the subject of an electronic investigation (R² = Me, *i*-Pr, *t*-Bu, CHPh₂, F).

Experimental section

General considerations

All manipulations involving air- and moisture-sensitive compounds were carried out under nitrogen atmosphere using standard Schlenk techniques. Toluene was refluxed over sodium and distilled under nitrogen prior to use. Methylaluminoxane (MAO, 1.46 M solution in toluene) and modified methylaluminoxane (MMAO, 1.93 M in n-heptane) were purchased from Akzo Nobel Corp. High-purity ethylene was purchased from Beijing Yansan Petrochemical Co. and used as received. Other reagents were purchased from Aldrich, Acros or local suppliers. FT-IR spectra were recorded on a Perkin-Elmer System 2000 FT-IR spectrometer. Elemental analysis was carried out using a Flash EA 1112 micro-analyzer. Molecular weights and molecular weight distributions (M_w/M_n) of the polyethylenes were determined by Gel Permeation Chromatography using a PL-GPC220 instrument at 150 °C with 1,2,4-trichlorobenzene as the solvent. The thermograms for the crystallization and melt process of the polymers were recorded using a differential scanning calorimeter (DSC, TA-Q2000) under a nitrogen atmosphere. Typically, a sample of about 5.0 mg was heated to 140 °C at a rate of 20 °C/min and kept for 2 min at 140 °C to remove the thermal history and then cooled at a rate of 20 °C/min to -40 °C. The ^{13}C NMR spectra of the polyethylenes were recorded on a Bruker DMX 300 MHz instrument at 135 °C in deuterated 1,1,2,2-tetrachloroethane- d_2 with TMS as an internal standard; δ values are given in ppm and J values in Hz. The compounds, α,α' -dioxo-2,3:5,6-bis(pentamethylene)pyridine,^{41,49-50} 2,4-dimethyl-6-benzhydrylaniline, 2-methyl-4,6-dibenzhydrylaniline, 2-ethyl-4,6-dibenzhydrylaniline, 2-isopropyl-4,6-dibenzhydrylaniline, 2-chloro-4,6-dibenzhydrylaniline, 2,6-dibenzhydryl-4-isopropylaniline, 2,6-dibenzhydryl-4-tertbutylaniline and 2,6-dibenzhydryl-4-fluoroaniline were prepared using literature procedures.⁵¹⁻⁵²

Preparation of [2,3:5,6-{C₄H₈C(N(2-R¹-4-R²-6-(CHPh₂)C₆H₂))}₂C₅HN]CoCl₂

(a) R¹ = R² = Me **Co1**. A mixture of α,α' -dioxo-2,3:5,6-bis(pentamethylene)pyridine (0.243 g, 1.0 mmol), 2,4-dimethyl-6-benzhydrylaniline (1.15 g, 4.0 mmol) and CoCl₂ (0.13 g, 1.0 mmol) in glacial acetic acid (10 ml) was stirred and heated to reflux for 6 h. Once cooled to room temperature, diethyl ether (30 mL) was added to precipitate a solid which was filtered and collected. This solid was then re-dissolved in methanol (40-50 mL) and the solution concentrated to a minimum volume (*ca.* 5 mL). Diethyl ether was added again to induce precipitation and the resulting solid collected by filtration and dried under reduced pressure to give **Co1** as a light green powder (0.48 g, 58%). FT-IR (KBr, cm⁻¹): 2938 (w), 2867 (w), 1599 (ν (C=N), s), 1549 (w), 1492 (s), 1449 (s), 1336 (m), 1257 (s), 1211 (m), 1152 (m), 1077 (m), 1031 (m), 967 (w), 783 (w), 747 (w), 701 (s). Anal. calc. for C₅₇H₅₅Cl₂CoN₃ (911.9): C, 75.08; H, 6.08; N, 4.61. Found: C, 75.06; H, 6.07; N, 4.60%.

(b) R¹ = Me, R² = CHPh₂ **Co2**. Using a similar procedure and molar ratios to that described for **Co1** but with 2-methyl-4,6-dibenzhydrylaniline as the amine, **Co2** was obtained as a light green powder (0.49 g, 40%). FT-IR (KBr, cm⁻¹): 2936 (w), 2866 (w), 1598 (ν (C=N), s), 1552 (w), 1493 (s), 1448 (s), 1341 (w), 1258 (s), 1208 (m), 1151 (m), 1077 (m), 1031 (m), 1003 (w), 967 (m), 850 (w), 818 (w), 741 (w), 697 (s). Anal. calc. for C₈₁H₇₁Cl₂CoN₃ (1216.3): C, 79.99; H, 5.88; N, 3.45. Found: C, 79.97; H, 5.88; N, 3.44%.

(c) R¹ = Et, R² = CHPh₂ **Co3**. Using a similar procedure and molar ratios to that described for **Co1** but with 2-ethyl-4,6-dibenzhydrylaniline as the amine, **Co3** was obtained as a light green powder (0.49 g, 40%). FT-IR (KBr, cm⁻¹): 2970 (w), 2873 (w), 1630 (m), 1600 (ν (C=N), s), 1576 (w), 1551 (w), 1490 (m), 1449 (s), 1378 (w), 1283 (w), 1255 (m), 1203 (m), 1172 (w), 1145 (w), 1075 (w), 1039 (w), 1006 (w), 974 (w), 922 (w), 897 (w), 861 (w), 742 (w), 698 (s) cm⁻¹. Anal. calc. for C₈₃H₇₅Cl₂CoN₃ (1244.37): C, 80.11; H, 6.08; N, 3.38. Found: C, 79.8; H, 5.88; N, 3.49%.

(d) $R^1 = i\text{-Pr}$, $R^2 = \text{CHPh}_2$ **Co4**. Using a similar procedure and molar ratios to that described for **Co1** but with 2-*iso*-propyl-4,6-dibenzhydrylaniline as the amine, **Co4** was obtained as a light green powder (0.49 g, 30%). FT-IR (KBr, cm^{-1}): 2934 (w), 2866 (w), 1598 ($\nu(\text{C}=\text{N})$, s), 1553 (w), 1493 (s), 1447 (s), 1339 (m), 1255 (s), 1208 (m), 1149 (m), 1076 (m), 1032 (m), 966 (w), 913 (m), 856 (w), 776 (w), 743 (w), 698 (s). Anal. calc. for $\text{C}_{85}\text{H}_{79}\text{Cl}_2\text{CoN}_3$ (1272.42): C, 80.24; H, 6.26; N, 3.30. Found: C, 79.80; H, 6.00; N, 3.38%.

(e) $R^1 = \text{Cl}$, $R^2 = \text{CHPh}_2$ **Co5**. Using a similar procedure and molar ratios to that described for **Co1** but with 2-chloro-4,6-dibenzhydrylaniline as the amine, **Co5** was obtained as a light green powder (0.423 g, 38%). FT-IR (KBr, cm^{-1}): 2935 (w), 2870 (w), 1598 ($\nu(\text{C}=\text{N})$, s), 1556 (w), 1494 (s), 1448 (s), 1339 (m), 1256 (s), 1224 (m), 1170 (m), 1077 (m), 1030 (m), 965 (w), 924 (m), 888 (w), 794 (w), 765 (w), 698 (s). Anal. calc. for $\text{C}_{79}\text{H}_{65}\text{Cl}_4\text{CoN}_3$ (1257.1): C, 75.48; H, 5.21; N, 3.34. Found: C, 75.65; H, 5.15; N, 3.34%.

(f) $R^1 = \text{CHPh}_2$, $R^2 = i\text{-Pr}$ **Co6**. Using a similar procedure and molar ratios to that described for **Co1** but with 2,6-dibenzhydryl-4-isopropylaniline as the amine, **Co6** was obtained as a light green powder (0.665 g, 52%). FT-IR (KBr, cm^{-1}): 2951 (w), 2866 (w), 1594 ($\nu(\text{C}=\text{N})$, s), 1548 (w), 1493 (s), 1447 (s), 1340 (m), 1255 (s), 1210 (m), 1172 (m), 1076 (m), 1031 (m), 964 (w), 930 (m), 862 (w), 794 (w), 765 (w), 698 (s). Anal. calc. for $\text{C}_{85}\text{H}_{79}\text{Cl}_2\text{CoN}_3$ (1272.4): C, 80.24; H, 6.26; N, 3.30. Found: C, 80.06; H, 6.25; N, 3.30%.

(g) $R^1 = \text{CHPh}_2$, $R^2 = t\text{-Bu}$ **Co7**. Using a similar procedure and molar ratios to that described for **Co1** but with 2,6-dibenzhydryl-4-*tert*-butyl aniline as the amine, **Co7** was obtained as a light green powder (0.533 g, 41%). FT-IR: 2948 (w), 2868 (w), 1595 ($\nu(\text{C}=\text{N})$, s), 1544 (w), 1491 (s), 1449 (s), 1337 (m), 1257 (s), 1210 (m), 1184 (m), 1078 (m), 1030 (m), 933 (m), 893 (m), 823 (m), 770 (m), 743 (m), 698 (s). Anal. calc. for $\text{C}_{87}\text{H}_{83}\text{Cl}_2\text{CoN}_3$ (1300.5): C 80.35, H 6.43, N 3.23. Found C 80.00, H 6.41, N 3.20%.

(h) $R^1 = \text{CHPh}_2$, $R^2 = \text{F}$ **Co8**. Using a similar procedure and molar ratios to that described for **Co1** but with 2,6-dibenzhydryl-4-fluorophenyl aniline as the amine, **Co8** was obtained as a light green powder (0.489 g, 40%). FT-IR: 2946 (w), 2869 (w), 1593 ($\nu(\text{C}=\text{N})$, s), 1545 (w), 1494 (s), 1444 (s), 1345 (m), 1260 (m), 1183 (s), 1158 (m), 1077 (m), 1030 (m), 969 (w), 935 (m), 865 (w), 790 (w), 765 (w), 699 (s). Anal. calc. for $\text{C}_{79}\text{H}_{65}\text{Cl}_2\text{CoF}_2\text{N}_3$ (1224.22): C, 77.51; H, 5.35; N, 3.43. Found: C, 77.45; H, 5.31; N, 3.45%.

Ethylene polymerization at 5/10 atm ethylene pressure

The autoclave was evacuated and backfilled with ethylene three times. When the required temperature was reached, the precatalyst (5 μmol) was dissolved in toluene (30 mL) in a Schlenk tube and injected into the autoclave containing ethylene (*ca.* 1 atm) followed by the addition of more toluene (30 mL). The required amount of co-catalyst (MAO and MMAO) and additional toluene were added successively by syringe taking the total volume of toluene to 100 mL. The autoclave was immediately pressurized with 5/10 atm. pressure of ethylene and the stirring commenced. After the required reaction time, the reactor was cooled with a water bath and the excess ethylene vented. Following quenching of the reaction with 10% hydrochloric acid in ethanol, the polymer was collected and washed with ethanol and dried under reduced pressure at 50 °C and weighed.

Ethylene polymerization at 1 atm ethylene pressure

The polymerization at 1 atm ethylene pressure was carried out in a Schlenk tube. Under an ethylene atmosphere (1 atm), **Co1** (5 μmol) was added followed by toluene (30 mL) and then the required amount of co-catalyst (MAO, MMAO) introduced by syringe. The solution was then stirred at 30 °C under an ethylene atmosphere (1 atm). After 30 min, the solution was quenched with 10% hydrochloric acid in ethanol. The polymer was washed with ethanol, dried under reduced pressure at 40 °C and then weighed.

X-ray Crystallographic Studies

The single-crystal X-ray diffraction studies of **Co1**, **Co6** and **Co8** were carried out on a Rigaku sealed Tube CCD (Saturn 724+) diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) at 173(2) K; cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least squares on F^2 . All non-hydrogen atoms were placed in calculated positions. Structural solution and refinement were performed by using the SHELXTL-97 package.⁵³⁻⁵⁴ The free solvents present within the single crystal were removed by using the SQUEEZE option of the crystallographic program PLATON.⁵³⁻⁵⁴ Details of the X-ray refinements are provided in Table1.

Table 1. Crystal data and structure refinement for **Co1**, **Co6** and **Co8**

	Co1	Co6	Co8
CCDC No.	1854922	1854923	1854924
Empirical formula	C ₅₇ H ₅₅ Cl ₂ CoN ₃	C ₈₅ H ₇₉ Cl ₂ CoN ₃	C ₇₉ H ₆₅ Cl ₂ CoF ₂ N ₃
F _w	911.87	1272.43	1224.17
T (K)	173.15(2)	173.15	293.00 (2)
Wavelength	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	P2 ₁ /c	P2 ₁ /c	P2 ₁ /c
a(Å)	10.2828(4)	24.108(5)	10.599(2)
b(Å)	26.5515(6)	15.504(3)	27.076(5)
c(Å)	19.0766(7)	20.334(4)	23.589(5)
α (°)	90.00	90.00	90.00
β (°)	104.488(4)	93.60(3)	101.95(3)
γ (°)	90.00	90.00	90.00
V(Å ³)	5042.7(3)	7585(3)	6623(2)
Z	4	4	4
D _{calcd} (mg m ³)	1.201	1.114	1.228
μ (mm ⁻¹)	0.485	0.340	0.391
F(000)	1916.0	2687.3	2556.0
Crystal size (mm)	0.213 × 0.064 × 0.043	0.137 × 0.094 × 0.053	0.421 × 0.105 × 0.087
θ range (°)	3.068 - 63.162	1.7 - 54.96	1.159 - 27.489
Limiting indices	-14 ≤ h ≤ 14 -36 ≤ k ≤ 36 -26 ≤ l ≤ 27	-30 ≤ h ≤ 31 -20 ≤ k ≤ 20 -25 ≤ l ≤ 26	-13 ≤ h ≤ 13 -35 ≤ k ≤ 35 -30 ≤ l ≤ 30
No. of rflns collected	84680	80235	77296
No. unique rflns [R(int)]	15695 (0.0903)	17362 (0.1018)	15123 (0.0572)
Completeness to θ (%)	93%	100%	99.6%
Data/restraints/params	15695 / 211 / 627	17362 / 0 / 823	15123 / 468 / 940

Goodness of fit on F^2	1.061	1.022	1.191
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0954$, $wR_2 = 0.2062$	$R_1 = 0.1649$, $wR_2 = 0.2616$	$R_1 = 0.0805$ $wR_2 = 0.1840$
R indexes (all data)	$R_1 = 0.1736$, $wR_2 = 0.2386$	$R_1 = 0.1935$ $wR_2 = 0.2779$	$R_1 = 0.0865$ $wR_2 = 0.1883$
Largest diff peak and hole ($e \text{ \AA}^{-3}$)	0.89 and -0.79	1.41 and -1.20	0.429 and -0.411

Results and discussion

Condensation of diketone α, α' -dioxo-2,3:5,6-bis(pentamethylene)pyridine with two equivalents of 2-(CHPh₂)-4-R¹-6-R²C₆H₂NH₂ (R¹ = Me, R² = Me; R¹ = Me, R² = CHPh₂; R¹ = Et, R² = CHPh₂; R¹ = *i*-Pr, R² = CHPh₂; R¹ = Cl, R² = CHPh₂; R¹ = CHPh₂, R² = *i*-Pr; R¹ = CHPh₂, R² = *t*-Bu; R¹ = CHPh₂, R² = F) in the presence of cobalt chloride gave, on work-up, [2,3:5,6-{C₄H₈C(N(2-R¹-4-R²-6-(CHPh₂)C₆H₂))}]₂C₅HN]CoCl₂ (R¹ = R² = Me **Co1**, R¹ = Me, R² = CHPh₂ **Co2**, R¹ = Et, R² = CHPh₂ **Co3**, R¹ = *i*-Pr, R² = CHPh₂ **Co4**, R¹ = Cl, R² = CHPh₂ **Co5**, R¹ = CHPh₂, R² = *i*-Pr **Co6**, R¹ = CHPh₂, R² = *t*-Bu **Co7**, R¹ = CHPh₂, R² = F **Co8**), in moderate yields (30 - 58%) (Scheme 1). The free ligands did not prove amenable to isolation and so the above template approach was implemented to access the complexes in one step; similar one pot approaches have been employed elsewhere.^{35,40-44,48} All complexes are air and moisture stable and have been characterized by infrared spectroscopy and elemental analysis. In addition, crystals of **Co1**, **Co6** and **Co8** have been the subject of single crystal X-ray diffraction studies.

	Co1	Co2	Co3	Co4	Co5	Co6	Co7	Co8
R ¹	Me	Me	Et	<i>i</i> -Pr	Cl	Ph ₂ CH	Ph ₂ CH	Ph ₂ CH
R ²	Me	Ph ₂ CH	Ph ₂ CH	Ph ₂ CH	Ph ₂ CH	<i>i</i> -Pr	<i>t</i> -Bu	F

Scheme 1 One-pot template route to **Co1 - Co8**

Single crystals of **Co1**, **Co6** and **Co8** suitable for the X-ray determinations were grown by slow diffusion of diethyl ether into a dichloromethane solution of the corresponding complex at ambient temperature. Perspective views of the complexes are shown in Figures 1, 2 and 3; selected bond distances and angles for all three are collected in Table 1. All the structures are similar and will be discussed together. Each consists of a single cobalt center surrounded by the three nitrogen atoms belonging to the bis(arylimino)-2,3:5,6-bis(pentamethylene)pyridine (aryl = 2,4-Me₂-6-(CHPh₂)C₆H₂ **Co1**, 2,6-(CHPh₂)₂-4-*i*-PrC₆H₂ **Co6**, 2,6-(CHPh₂)₂-4-FC₆H₂ **Co8**) and two chlorides to complete a five-coordinate geometry best described as distorted square-pyramidal geometry. The three nitrogen and Cl2 atoms form the basal plane with Cl1 occupying the apical position, while the cobalt atoms lie at a distance of 0.497 Å (**Co1**), 0.567 Å (**Co6**) and 0.468 Å (**Co8**) above this basal plane; similar arrangements have been found in previously reported analogues.^{35,39,41,43,45-46,55-56} Of the three nitrogen donors within the tridentate ligand, the central pyridine nitrogen forms the shortest Co-N bond distance [2.044(3) Å **Co1**, 2.052(5) Å **Co6**, 2.070(2) Å **Co8**] and indeed compares favorably with those found in **A** (2.051 - 2.056 Å),^{1-2,4,6} **B** (2.037 Å),³⁵ **C** (2.082 Å)⁴¹ **D** (2.072 - 2.079 Å)⁴⁵, **E** (2.087 Å)⁴⁶ and **F** (2.072 - 2.079 Å).⁴⁸ The two exterior Co-N_{imine} distances [2.187(3), 2.178(3) Å **Co1**, 2.162(5), 2.166(5) Å **Co6**; 2.164(2), 2.173(3) Å **Co8**] are similar, despite the more demanding 2,6-dibenzhydryl N-aryl substitution in **Co6** and **Co8**. Within the two 5-membered chelate rings, the N2-Co1-N1 and N1-Co1-N3 bond angles are close in value [75.96(12)°, 75.30(12)° **Co1**; 74.9(2)°, 74.9(2)° **Co6**; 74.99(9)°, 74.66(10)° **Co8**], N(2)-Co(1)-N(3) and comparable with related structures.^{35-37,39,41,43,45,47} The N(1)-C(15)-C(1)-N(3) and N(2)-C(13)-C(14)-N(1) torsion angles [-13.83°, -17.05° (**Co1**), 3.63°, 0.05° (**Co6**), -6.82°, 10.73° (**Co8**)] highlight the deviation from co-planarity between the pyridine ring and the neighboring imine vectors. As expected the saturated sections of the fused seven-membered rings, C2-C3-C4-C5 and C9-C10-C11-C12, adopt puckered configurations on account of the sp³-hybridized carbon atoms. For **Co1** the N-aryl groups are inclined at an angle of 86.82°_{av} with respect to the imine vectors while in **Co6** and **Co8** the corresponding angles decrease

to 82.14°_{av} and 78.3°_{av} , likely reflecting the presence of the more sterically demanding 2,6-benzhydryl substitution in **Co6** and **Co8**. There are no intermolecular contacts of note.

Figure 1 ORTEP representations of **Co1**. Thermal ellipsoids are shown at 30% probability and hydrogen atoms have been omitted for clarity.

Figure 2 ORTEP representations of **Co6**. Thermal ellipsoids are shown at 30% probability and the hydrogen atoms have been omitted for clarity.

Figure 3 ORTEP representations of **Co8**. Thermal ellipsoids are shown at 30% probability and the hydrogen atoms have been omitted for clarity.

Table 2 Selected lengths (Å) and angles (°) for **Co1**, **Co6** and **Co8**

	Co1	Co6	Co8
Bond lengths [Å]			
Co(1)-N(1)	2.044(3)	2.052(5)	2.070(2)
Co(1)-N(2)	2.187(3)	2.162(5)	2.164(2)
Co(1)-N(3)	2.178(3)	2.166(5)	2.173(3)
Co(1)-Cl(1)	2.2904(12)	2.295(2)	2.3128(11)
Co(1)-Cl(2)	2.2489(12)	2.2595(18)	2.2531(9)
N(3)-C(1)	1.285(5)	1.295(8)	1.290(4)
N(2)-C(13)	1.358(13)	1.288(8)	1.296(4)
N(1)-C(14)	1.330(5)	1.352(8)	1.336(4)
N(1)-C(15)	1.335(4)	1.312(8)	1.336(4)
Bond angles [°]			
N(2)-Co(1)-N(3)	144.10(12)	141.8(2)	144.21(9)
N(1)-Co(1)-N(3)	75.30(12)	74.9(2)	74.66(10)
N(2)-Co(1)-N(1)	74.96(12)	74.9(2)	74.99(9)
N(3)-Co(1)-Cl(1)	99.34(8)	104.88(14)	98.52(7)
N(3)-Co(1)-Cl(2)	98.16(9)	97.37(14)	100.20(7)
N(2)-Co(1)-Cl(1)	92.97(11)	98.79(15)	100.68(7)
N(2)-Co(1)-Cl(2)	96.20(9)	98.78(14)	100.10(7)
Cl(1)-Co(1)-Cl(2)	115.72(8)	112.10(4)	119.52(5)
C(1)-N(3)-Co(1)	114.7(2)	115.4(4)	115.3(2)
C(13)-N(2)-Co(1)	116.4(5)	114.3(4)	115.7(2)

Further support for the structural composition of **Co1** – **Co8** was provided by the microanalytical and IR data, the latter revealing imine absorptions around 1600 cm⁻¹ which are typical of cobalt(II)-coordinated imine nitrogens.^{1,41,45}

Catalyst evaluation for ethylene polymerization

To explore the performance of **Co1** - **Co8** in ethylene polymerization, two types of co-catalyst were selected for their activation namely methylaluminoxane (MAO) and modified methylaluminoxane (MMAO). Indeed, scrutiny of the literature reveals that these two aluminoxanes have proved the most suitable co-catalyst for activating related cobalt precatalysts.^{1-6,35-48} To determine the effectiveness of each, we initiated two separate studies to investigate the performance of the eight structurally distinct precatalysts. However, in both studies an optimization of the conditions was initially performed using **Co1** as the test precatalyst. All polymeric material has been characterized by gel permeation chromatography (GPC), differential

scanning calorimetry (DSC) and in selected cases by high temperature ^{13}C NMR spectroscopy; GC was also used to assess for the formation of any oligomeric products.

Optimization of Co1/MAO for ethylene polymerization

To allow an optimization of Co1/MAO as a catalyst for ethylene polymerization, the molar ratio of MAO to precatalyst (Al/Co), reaction temperature and run time were all systematically varied. Typically, the runs were performed in toluene under 10 atm C_2H_4 . Firstly, the Al/Co molar ratio was varied from 500 to 2500 with the temperature set at 30 °C and the polymerization run time at 30 minutes (entries 1 - 7, Table 3). A peak in activity of 1.31×10^6 g (PE) mol^{-1} (Co) h^{-1} was observed with an Al/Co ratio of 1000 (entry 3, Table 3). As the ratio was increased above 1000, the catalytic activities steadily decreased reaching a minimum value of 0.92×10^6 g (PE) mol^{-1} (Co) h^{-1} at 2500. In addition, the molecular weights gradually dropped from 45.0 to 33.6 kg mol^{-1} which is likely due to increased chain transfer to aluminum on increasing the amount of alkyl aluminum reagent (Figure 4).^{4,40-42} On the other hand, the molecular weight distribution remained remarkably narrow ($M_w/M_n = 1.41 - 1.74$) across the range of Al/Co molar ratios.

Table 3 Ethylene polymerization results using Co1 with MAO as co-catalyst^a

Entry	Al/Co	T (°C)	t (min)	Yield (g)	Activity ^b	M_w^c	M_w/M_n^c	T_m (°C) ^d
1	500	30	30	0.93	0.37	45.0	1.72	133.8
2	750	30	30	2.15	0.86	42.0	1.64	134.4
3	1000	30	30	3.28	1.31	37.9	1.74	134.6
4	1250	30	30	3.10	1.24	35.5	1.54	133.7
5	1500	30	30	3.06	1.22	34.3	1.41	135.1
6	2000	30	30	2.87	1.14	33.9	1.41	133.7
7	2500	30	30	2.32	0.92	33.6	1.46	133.4
8	1000	20	30	2.51	1.00	43.8	1.67	136.0
9	1000	40	30	2.20	0.88	28.6	2.09	133.8
10	1000	50	30	2.00	0.80	18.3	1.49	128.1
11	1000	60	30	1.45	0.58	7.0	2.30	125.4
12	1000	70	30	0.28	0.11	2.0	1.54	125.9
13	1000	80	30	trace	-	-	-	-
14 ^e	1000	30	30	1.47	0.58	25.6	2.36	132.2
15 ^f	1000	30	30	0.25	0.10	3.7	2.50	125.5
16	1000	30	5	0.65	1.56	25.3	1.53	132.2
17	1000	30	15	1.71	1.37	25.4	1.54	133.8
18	1000	30	45	4.66	1.24	58.8	2.78	135.2
19	1000	30	60	4.75	0.95	77.1	3.48	134.2

^a Conditions: 5.0 μmol of **Co1**; 100 mL toluene, 10 atm C_2H_4 .

^b Expressed in units of $10^6 \text{ g(PE) mol}^{-1} (\text{Co}) \text{ h}^{-1}$.

^c Determined by GPC, and M_w in kg mol^{-1} .

^d Determined by DSC.

^e 5 atm ethylene.

^f 1 atm ethylene.

Figure 4 GPC curves for the polyethylenes obtained using **Co1**/MAO with various Al/Co ratios (entries 1 – 7, Table 3)

By varying the temperature from 20 to 80 °C (entries 8, 3, 9 - 13, Table 3) with the Al/Co molar ratio kept at 1000, the maximum activity of $1.31 \times 10^6 \text{ g (PE) mol}^{-1} (\text{Co}) \text{ h}^{-1}$ could be again identified at 30 °C. However, above 30 °C the activity of **Co1**/MAO steadily dropped reaching a minimum value at 80 °C at which point only a trace amount of polymer could be isolated (entry 13, Table 3). Moreover, the molecular weights of the polyethylenes lowered from 43.8 to 2.0 kg mol^{-1} as the temperature was raised, an observation that can be attributed to the higher rate of chain termination at higher temperature (Figure 5).^{4,42} On the other hand, the molecular weight distribution remained narrow (M_w/M_n : 1.49 - 2.80) over the temperature range consistent with an active species displaying single-site behavior.

Figure 5 GPC curves for the polyethylenes obtained using **Co1**/MAO at different reaction temperatures (entries 8, 3, 9 - 13, Table 3)

With the aim to gain some information as to the lifetime of the active species and the influence of the reaction time on the polymer properties, the polymerizations ($\text{Al/Co} = 1000$, $T = 30\text{ }^{\circ}\text{C}$) were conducted over various run times between 5 and 60 minutes (entries 3, 16 - 19, Table 3). The topmost activity of $1.56 \times 10^6\text{ g (PE) mol}^{-1}\text{ (Co) h}^{-1}$ was observed after 5 minutes (entry 16, Table 3), while prolonging the reaction time from 15 to 60 minutes led to a gradual drop in activity from 1.37 to $0.95 \times 10^6\text{ g (PE) mol}^{-1}\text{ (Co) h}^{-1}$. This would suggest the active species was rapidly formed on addition of MAO then gradually deactivated over time. Conversely, the molecular weight of the polymer increased from **25.3** to **77.1** kg mol^{-1} over the course of the reaction, highlighting that despite apparent deactivation there were sufficient active species present to maintain chain propagation (Figure 6).^{41,57} In terms of the molecular weight distribution, this showed some modest increase over time (M_w/M_n : 1.53 to 3.48), but nevertheless remained reasonably narrow even after one hour.

The effect of ethylene pressure on polymerization performance of **Co1**/MAO was also investigated. On lowering the pressure from 10 to 5 atm, the activity decreased by more than half from $1.31 \times 10^6\text{ g (PE) mol}^{-1}\text{ (Co) h}^{-1}$ to $0.58 \times 10^6\text{ g (PE) mol}^{-1}\text{ (Co) h}^{-1}$ (entries 2, 14, Table 3). Further reduction in the pressure to 1 atm saw the activity drop to $0.10 \times 10^6\text{ g (PE) mol}^{-1}\text{ (Co) h}^{-1}$ (entry 15, Table 3). Likewise, the molecular weight of the polymer decreased with reduced

ethylene pressure from 37.9 to 3.7 kg mol⁻¹, while a narrow molecular weight distribution (M_w/M_n : 1.74 - 2.50) was a feature at all three pressures.

Figure 6 GPC curves for the polyethylenes obtained using **Co1**/MAO at different run times (entries 16 – 19, Table 3)

Optimization of **Co1**/MMAO for ethylene polymerization

As with **Co1**/MAO, a similar optimization process was performed this time using **Co1** in combination with MMAO at 10 atm C₂H₄; the results are compiled in Table 4. With the temperature at 30 °C and the run time at 30 minutes, the Al/Co molar ratio was varied from 500 to 2500 (entries 1 - 7, Table 4) leading to the highest activity of 1.63×10^6 g (PE) mol⁻¹ (Co) h⁻¹ reached with a ratio of 1000 (entry 3, Table 4); this compares to 1.31×10^6 g (PE) mol⁻¹ (Co) h⁻¹ for **Co1**/MAO under comparable conditions. Raising this ratio above 1000 resulted in a slow decrease in performance from 1.59×10^6 g (PE) mol⁻¹ (Co) h⁻¹ (Al/Co = 1250) to 1.33×10^6 g (PE) mol⁻¹ (Co) h⁻¹ (Al/Co = 2500). In addition, the molecular weight of the polymers gradually decreased from 64.8 to 42.7 kg mol⁻¹ over the molar ratio range (Figure 7), which is notably higher than that seen with **Co1**/MAO (45.0 to 33.6 kg mol⁻¹). It uncertain as to this difference between activators but may derive from higher amounts of AlMe₃ that are present in commercial samples of MMAO as compared to that in MAO. By contrast, the molecular weight distribution was particularly narrow with little variation across the range (M_w/M_n : 1.63 - 1.33).

Table 4 Ethylene polymerization results of **Co1** with MMAO as co-catalyst^a

Entry	Al/Co	T (°C)	t (min)	Yield (g)	Activity ^b	M_w^c	M_w/M_n^c	T_m (°C) ^d
1	500	30	30	3.64	1.46	64.8	3.02	135.2
2	750	30	30	3.77	1.51	64.1	3.60	134.8
3	1000	30	30	4.06	1.63	50.3	1.84	133.8
4	1250	30	30	3.97	1.59	46.5	1.78	134.0
5	1500	30	30	3.54	1.42	46.3	1.94	134.4
6	2000	30	30	3.45	1.38	45.0	1.75	134.0
7	2500	30	30	3.32	1.33	42.7	1.35	134.2
8	1000	20	30	3.98	1.60	129.2	2.50	135.1
9	1000	40	30	4.68	1.87	12.8	2.68	130.7
10	1000	50	30	3.85	1.54	6.6	2.32	127.9
11	1000	60	30	2.75	1.10	2.9	1.90	124.2
12	1000	70	30	1.50	0.60	1.7	1.64	122.5
13	1000	80	30	0.36	0.14	1.7	1.49	119.4
14	1000	40	5	0.89	0.36	7.9	1.57	128.9
15	1000	40	15	2.15	2.87	12.6	2.03	131.0
16	1000	40	45	5.16	1.37	22.3	1.64	131.9
17	1000	40	60	6.44	1.29	23.5	1.69	133.1
18 ^e	1000	40	30	1.92	0.76	5.6	1.58	129.1

^a Conditions: 5.0 μmol of **Co1**; 100 mL toluene, 10 atm C_2H_4 .^b Expressed in units of $10^6 \text{ g(PE) mol}^{-1} (\text{Co}) \text{ h}^{-1}$.^c Determined by GPC, and M_w in kg mol^{-1} .^d Determined by DSC.^e 5 atm ethylene. **Figure 7** GPC curves for the polyethylenes obtained using **Co1**/MMAO with various Al/Co ratios (entries 1 – 7, Table 4)

With the Al/Co molar ratio maintained at 1000, the run temperature was varied between 20 and 80 °C (entries 3, 8 - 13, Table 4). The optimum reaction temperature was observed at 40 °C with an activity of 1.87×10^6 g (PE) mol⁻¹ (Co) h⁻¹ (entry 9, Table 4). Above 40 °C the catalytic activity steadily decreased reaching a minimum value of 0.14×10^6 g (PE) mol⁻¹ (Co) h⁻¹ at 80 °C; nonetheless this value is significantly higher than that observed with **Co1**/MAO at the same temperature (see entry 13, Table 4). The molecular weight of the polyethylene was found to rapidly drop from 129.2 kg mol⁻¹ at 20 °C to 12.8 kg mol⁻¹ at 40 °C and then assume a more gradual decline reaching a minimum value of 1.7 kg mol⁻¹ at 80 °C (Figure 8). Across the entire temperature range, the molecular weight distribution remained narrow (M_w/M_n : 1.49 - 2.68). In comparison with the variable temperature runs performed with **Co1**/MAO, the molecular weight of the polymers produced using **Co1**/MMAO was generally higher.

Figure 8 GPC curves for the polyethylenes obtained using **Co1**/MMAO at different reaction temperatures (entries 3, 8 – 13, Table 4)

The effect of time on the catalytic activity and polymer properties was then investigated using **Co1**/MMAO at 40 °C with the Al/Co molar ratio at 1000. The polymerizations were conducted over 5, 15, 30, 45 and 60 minute run times resulting in the highest activity of 2.87×10^6 g (PE) mol⁻¹ (Co) h⁻¹ being achieved after 15 minutes (entries 14 - 15, 9, 16 - 17, Table 4). Notably, this value compares to just 5 minutes with MAO which highlights the slower catalyst induction period needed with MMAO. However, extending the run time beyond 15 minutes

results in slow catalyst deactivation with the activity reaching a minimum value of 1.29×10^6 g (PE) mol⁻¹ (Co) h⁻¹ after one hour.^{39,57} Nevertheless, the molecular weight of the polymer continued to rise with time reaching a maximum of 23.5 kg mol⁻¹ after one hour (Figure 9), while a narrow molecular weight distribution was observed with all these runs (M_w/M_n : 1.57 - 2.68).

Reducing the ethylene pressure from 10 to 5 atm saw the activity drop from 1.87×10^6 g (PE) mol⁻¹ (Co) h⁻¹ to 0.76×10^6 g (PE) mol⁻¹ (Co) h⁻¹ (entries 9, 18 Table 4). On the other hand, the molecular weight of the polymer fell from 12.8 kg mol⁻¹ at 10 atm to 5.6 kg mol⁻¹ at 5 atm, while little variation in the polydispersity was observed (M_w/M_n : 1.58 – 2.68).

Figure 9 GPC curves for the polyethylenes obtained using **Co1**/MMAO at different reaction times (entries 14 – 17, Table 4)

For the purposes of comparison, the activity and molecular weight data for the polymer generated using **Co1** are shown in Figure 10 alongside that obtained for structurally related fused examples of **C**, **E** and **F** (all polymerizations were performed at 10 atm C₂H₄ over 30 minutes using MMAO as co-catalyst). Two key points emerge from inspection of the figure. Firstly, the presence of a *ortho*-benzhydryl group in **Co1** has the effect of increasing the molecular weight of the polymer when compared to **C** but not as significantly as that seen for the *ortho*-cyclohexyl derivative **E**. On the other hand, the catalytic activity for **Co1** is slightly lower than that observed with **C** and **E** but significantly higher when compared to the oligomerization *N,N,O*-precatalyst **F**.

Figure 10 Comparative catalytic performance of **Co1** (entry 9, Table 3) with cobalt-containing **C**,⁴¹ **E**⁴⁶ and **F**⁴⁸ (Chart 1); all polymerizations were recorded at 10 atm C_2H_4 , 30 min using MMAO as co-catalyst. Other comparative data can be found in the SI.

General catalytic screen of **Co1** – **Co8** with MAO and MMAO

With the optimal conditions established for **Co1**/MAO [Al/Co ratio = 1000, temperature = 30 °C and run time = 30 minutes, 10 atm C_2H_4] and **Co1**/MMAO [Al/Co ratio = 1000, run temperature 40 °C and run time = 30 minutes], the remaining seven precatalysts were investigated using the corresponding set of parameters for each co-catalyst; the results of these polymerization tests along with those for **Co1** are collected in Table 5.

Several points can be identified by examination of the data. Firstly, with MAO as co-catalyst, **Co1** - **Co5** all displayed good activities with their values falling in the range $1.31 - 0.15 \times 10^6 \text{ g (PE) mol}^{-1} (\text{Co}) \text{ h}^{-1}$ (entries 1 - 5, Table 5). Similarly with MMAO, **Co1** - **Co5** showed good activity and indeed slightly higher than that observed with MAO ($1.87 - 0.10 \times 10^6 \text{ g (PE) mol}^{-1} (\text{Co}) \text{ h}^{-1}$; entries 9 - 26, Table 5). By contrast, **Co6** – **Co8** gave only trace amounts of polymer irrespective of the co-catalyst employed (entries 6 - 9, 14 -15, Table 5). In terms of the relative performance of the precatalysts, the same order was observed for both activators namely: **Co1** > **Co5** > **Co2** > **Co3** > **Co4** >> **Co6** ~ **Co 7** ~ **Co8** (Figure 11). Clearly, steric and electronic properties of the N-aryl groups are influential on catalytic activity.⁵⁸ With regard to steric effects,

the best activities were achieved by pairing the least bulky *ortho*-R¹ substituents *e.g.*, methyl (**Co1**) alongside an *ortho*-benzhydryl group.^{2-3,34} On the other hand, by the pairing of two *ortho*-benzhydryl groups (**Co6** – **Co8**) leads to too much steric protection and hence prevents efficient approach of the ethylene monomer to the metal center and in-turn negligible activities.^{13,37} The effects of electronic changes are more subtle and may explain the higher activity of **Co1** over **Co2** in which the *para*-substituent is either a methyl or a benzhydryl, respectively. Similarly, the superior activity of *ortho*-chloro **Co5** when compared to *ortho*-alkyls **Co2** – **Co4** may have an electronic origin as well as steric.

Secondly, the molecular weight of the polymers obtained using **Co1** - **Co5**/MAO range from 28.7 – 53.3 kg mol⁻¹ which is comparable to 12.3 – 59.4 kg mol⁻¹ obtained with **Co1** - **Co5**/MMAO (entries 1 – 5, 9 – 13, Table 5). In comparison with previously reported **C** (Chart 1) which incorporate less sterically bulky aryl groups (Ar = 2,6-Me₂Ph, 2,6-Et₂Ph, 2,6-*i*-Pr₂Ph, 2,4,6-Me₂Ph, 2,6-Et₂-4-MePh),⁴¹ the molecular weights in this study are generally an order of magnitude higher. This observation can be accredited to the *ortho*-bulky substituent more effectively preventing chain termination in manner similar to that previously reported.^{13,46} Indeed, the more bulky benzhydryl/*i*-Pr and benzhydryl/Cl *ortho*-pairings in **Co4** and **Co5** afford the highest molecular weight of the **Co1** – **Co5** series. As a general observation, the molecular weight distributions are in all runs narrow regardless of precatalyst and co-catalyst.

Table 5 Ethylene polymerization results using **Co1** – **Co8** with either MAO or MMAO as co-catalyst^a

Entry	Precat.	Co-cat.	Al/Co	T (°C)	t (min)	Yield (g)	Activity ^b	<i>M_w</i> ^c	<i>M_w</i> / <i>M_n</i> ^c	<i>T_m</i> (°C) ^d
1	Co1	MAO	1000	30	30	3.28	1.31	37.9	1.74	134.6
2	Co2	MAO	1000	30	30	1.99	0.79	33.8	1.78	132.3
3	Co3	MAO	1000	30	30	1.30	0.52	28.7	2.06	131.2
4	Co4	MAO	1000	30	30	0.37	0.15	53.3	1.38	128.0
5	Co5	MAO	1000	30	30	3.12	1.25	44.3	1.62	133.7
6	Co6	MAO	1000	30	30	trace	-	-	-	-
7	Co7	MAO	1000	30	30	trace	-	-	-	-
8	Co8	MAO	1000	30	30	trace	-	-	-	-
9	Co1	MMAO	1000	40	30	4.68	1.87	12.8	2.68	130.7
10	Co2	MMAO	1000	40	30	1.60	0.64	12.3	1.73	130.3
11	Co3	MMAO	1000	40	30	1.10	0.44	17.6	1.52	131.7
12	Co4	MMAO	1000	40	30	0.24	0.10	51.3	1.35	130.0
13	Co5	MMAO	1000	40	30	3.89	1.56	59.4	1.59	134.1
14	Co6	MMAO	1000	40	30	trace	-	-	-	-

15	Co7	MMAO	1000	40	30	trace	-	-	-
16	Co8	MMAO	1000	40	30	trace	-	-	-

^a Conditions: 5.0 μmol of precatalyst; 100 mL toluene, 10 atm ethylene.

^b Values in units of $10^6 \text{ g(PE) mol}^{-1} (\text{Co}) \text{ h}^{-1}$.

^c Determined by GPC, and M_w in kg mol^{-1} .

^d Determined by DSC.

Figure 11 Relative catalytic activity observed for **Co1** - **Co8** with the two different activators

Thirdly, the polymers generated using **Co1** – **Co5**/MAO and **Co1** – **Co5**/MMAO show similar melt temperatures falling in the range 128.0 – 134.6 °C (entries 1 - 5, 9 -13, Table 5), values which are characteristic of highly linear polyethylenes. To further investigate the polymer structure, representative samples prepared using **Co1**/MAO and **Co1**/MMAO were the subject of high-temperature $^1\text{H}/^{13}\text{C}$ NMR studies (recorded at 135 °C in deuterated 1,1,2,2-tetrachloroethane- d_2).

The ^{13}C NMR spectrum for the sample synthesized using **Co1**/MAO (entry 1, Table 5) revealed an intense peak at δ 30.0 for the $-(\text{CH}_2)_n-$ repeat in a linear polymer along with weaker upfield peaks (δ 32.20 (C_3), 22.91 (C_2), 14.35 (C_1)) that can be assigned to a saturated n -propyl end-group (Figure 12). Closer examination of the downfield region shows two very weak peaks between δ 140 – 110 that can be attributed to a vinyl end-group. The presence of this unsaturation

would suggest there is some vinyl-terminated polyethylene in the sample but based on the relative intensities of the methyl and CH₂=CH resonances, a fully saturated polymer is likely an additional component. This finding is corroborated in the ¹H NMR spectrum which reveals downfield vinylic protons for a and b integrating to 2 and 1, respectively, along with an upfield methyl end group at δ 0.97 integrating to *ca.* 9H (see insert in Figure 12), the latter high intensity signal is supportive of the co-existence of a fully saturated polymer.^{39,40} Overall these findings point towards both β-H elimination and transfer to aluminum being operative and competitive with MAO as co-catalyst.^{40,}

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Figure 12 ¹³C NMR spectrum of the polyethylene obtained using **Co1**/MAO (entry 1, Table 3) including an insert of the ¹H NMR spectrum; recorded in 1,1,2,2-tetrachloroethane-*d*₂ at 135 °C

For the polymer sample obtained using **Co1**/MMAO (entry 9, Table 5), the ¹³C NMR spectrum again reveals a high intensity peak around δ 30.00, in accord with a linear polyethylene (Figure 13). Likewise, upfield signals corresponding to an *n*-propyl end-group (C₁, C₂ and C₃) can be clearly seen while less intense vinylic carbons can be observed in the downfield region.^{35,42,45} Once again it would appear that both chain transfer to aluminum and β-H elimination are operating as competitive termination pathways. Furthermore, no evidence for *iso*-butyl end-groups could be detected highlighting the preference for the polymerization to undergo termination by chain transfer to AlMe₃ rather than Al(*i*-Bu)₃ and its derivatives present in MMAO.

Figure 13 ^{13}C NMR spectrum of the polyethylene obtained using **Co1**/MMAO (entry 9, Table 4); recorded in 1,1,2,2-tetrachloroethane- d_2 at 135 °C

Conclusions

A one-pot template approach has been successfully employed to generate the sterically and electronically distinct cobalt(II) chloride chelates, **Co1** – **Co8**, in reasonable yield. Full characterization of the complexes has been undertaken including in three cases by single crystal X-ray diffraction. On activation with MMAO or MAO, **Co1** – **Co5** exhibited high activity for ethylene polymerization and produced low molecular weight, highly linear polyethylenes exhibiting narrow molecular weight distributions. **Importantly, the molecular weight is higher than in their less sterically bulky counterparts (C and F Chart 1), highlighting the beneficial effect of benzhydryl substitution on chain propagation. On the other hand, the molecular weight obtained is not as high as that seen for *ortho*-cyclohexyl E.** End-group analysis of the polymers formed using either **Co1**/MAO or **Co1**/MMAO provided evidence for both β -hydrogen elimination and chain transfer to aluminum being operative during chain termination. By stark contrast, **Co6** - **Co8** when activated with either aluminoxane co-catalyst gave only trace amounts of polymer. In terms of relative performance, the complexes containing the least bulky benzhydryl/ R^1 *ortho*-pairings favored higher activities while the highest molecular weight polymer could be obtained be with a more bulky combination.

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